

Proximity effects induced by a gold layer on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films

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We report about $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ single crystal manganite thin films in interaction with a gold capping layer. With respect to uncoated manganite layers of the same thickness, Au-capped 4 nm-thick manganite films reveal a dramatic reduction ($\simeq 185$ K) of the Curie temperature T_C and a lower saturation low-temperature magnetization M_0 . A sizeable T_C reduction ($\simeq 60$ K) is observed even when an inert SrTiO_3 layer is inserted between the gold film and the 4 nm-thick manganite layer, suggesting that this effect might have an electrostatic origin.

The perovskite manganites of composition $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) have attracted a considerable interest because of the interplay between spin, charge, orbital, and lattice degrees of freedom in these materials, leading to a large variety of magnetic and electronic properties, such as colossal magnetoresistance.¹ The half-metallic character of manganites with $\text{A} = \text{Sr}, \text{Ca}$ is particularly relevant for applications in spin electronics where sources and detectors of highly polarized electron currents are required.

The electric and magnetic properties of manganites are extremely sensitive to the concentration of free carriers. These properties can be varied not only by hole-doping the material, but also by designing a heterostructure where light or an externally applied electric field might effectively modulate the carrier concentration.² Attempts to incorporate p -doped manganites in heterostructures with n -type conductors have demonstrated the possibility to control the carrier concentration and tune the intrinsic magnetic properties of the manganite layer through the modulation of interfacial electronic bands either with external bias voltages or carrier injection.^{3,4,5,6} Modulation of the transport and magnetic properties of epitaxial manganite films has also been obtained in field-effect devices, where a voltage is applied to a metal^{7,8,9} or ferroelectric^{10,11,12,13,14,15,16} gate electrode.

The presence of an interface represents, by itself, a significant perturbation of the electronic properties of perovskite manganites.² The interface with a metal is known to affect the chemical and electronic environment of strongly correlated oxides (a wide group of materials where electron-electron correlations play a fundamental role and that includes manganites), and can change basic electronic parameters, such as the Hubbard energy U , the electronic bandwidths, or the exchange energies.¹⁷ Nevertheless, the impact of the creation of a manganite/metal interface has been scarcely investigated,¹⁸ although its understanding is a fundamental step in the study of the effects taking place when other perturbations, such as electric fields, are applied to the heterostructure.

In the following, we report about the dramatic effects that depositing a metal layer on a $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

(LSMO) thin film has on the manganite magnetic properties. Since bulk LSMO is metallic at the $x = 0.33$ Sr doping concentration, band bending cannot take place throughout an extensive space charge region, contrary to what happens in the insulating manganite phases. Therefore, the interface with a different material is expected to influence the LSMO electronic and magnetic properties only over a very short length scale. It is thus essential to grow high quality thin LSMO layers forming very sharp interfaces with the metal. A noble metal is the most obvious choice as a partnering material, in the attempt to reduce chemical interdiffusion and interface reactions. Aluminium, for instance, drains oxygen from the manganite, altering its stoichiometry and strongly affecting the junction resistance vs. temperature dependence.¹⁹

Thin single crystal LSMO films (thickness t_{LSMO} between 4 and 12 nm) were deposited on SrTiO_3 (STO) by pulsed laser deposition using a tripled Nd:YAG laser (wavelength = 355 nm). The laser fluence was 1.4 J/cm² with a repetition rate equal to 2 Hz. The sample temperature and oxygen pressure were 973 K and 0.29 mbar, respectively. The surface roughness was characterized by Atomic Force Microscopy (AFM) and proved to be $\simeq 0.2$ nm root-mean-square, with a very small number of droplets covering less than 1% of the sample area. The LSMO deposition rate was calibrated by X-ray reflectometry, so that the estimated error in the thickness is lower than 0.2 nm.

All the LSMO thin films reproduce the characteristic metal-to-insulator transition [see Fig. 1(a)] typical of bulk LSMO. The temperature T_p at which the resistivity maximum is observed decreases with the LSMO film thickness, as discussed in Ref. 14. From the thickness dependence of the LSMO layer conductance [Fig. 1(b)] one can see that LSMO becomes electrically insulating below a critical thickness of the order of ≈ 3 nm, in agreement with Ref. 14. Anyway, the presence of a maximum in the resistivity vs. temperature dependence in Fig. 1(a) ensures that even the LSMO thin films with $t_{\text{LSMO}} = 4$ nm cannot be considered as electrically dead.¹⁴

The sample magnetization M as a function of the temperature T has been determined by a Superconducting Quantum-Interference Device (SQUID) and is re-

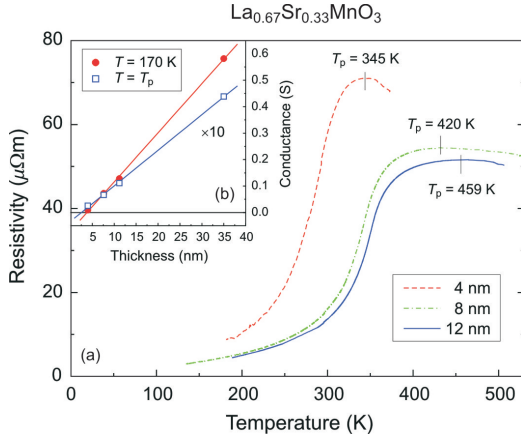


FIG. 1: (color online) (a) Temperature dependence of the resistivity in thin LSMO films with thickness equal to 4, 8, and 12 nm, measured in the four-probe configuration. (b) LSMO conductance as a function of the LSMO film thickness, at $T = 170\text{ K}$ and at $T = T_p$. The lines in the inset are linear fits to the data points.

ported in Fig. 2 for LSMO thin films with thickness $t_{\text{LSMO}} = 4\text{ nm}$ [Fig. 2(a)] and $t_{\text{LSMO}} = 8\text{ nm}$ [Fig. 2(b)]. The Curie temperature T_C is obtained as the temperature corresponding to the higher temperature inflection point of $M(T)$. In agreement with the observed trend of T_p , T_C is lower than the bulk value and decreases with the film thickness. We also note that the T_p reduction we observe by varying t_{LSMO} from 8 to 4 nm is more pronounced than the reduction of T_C . This indicates that the magnetic and electric transitions do not coincide, as highlighted in Ref. 20, and suggests that in thin LSMO films the transport properties are more affected than the magnetic ones.

Subsequently, we have studied the effect of depositing a thin (2 nm-thick) gold layer on top of LSMO films prepared as described above. Au has been evaporated from a Knudsen cell (pressure during deposition $\simeq 10^{-9}$ mbar). AFM does not measure any degradation of the surface roughness after Au deposition. Transport measurements across the Au/LSMO interfaces evidence an ohmic (non rectifying) behavior.

The effects of the Au capping on both the LSMO Curie temperature and the saturation magnetization M_0 at low temperature ($T = 5\text{ K}$) are noteworthy, as seen from Fig. 2 and Table I, where values of T_C , M_0 , and ΔT_C (the shift of the Au-capped LSMO layer Curie temperature with respect to the same thickness uncapped layer) are listed. A sizeable reduction of T_C and M_0 is observed for $t_{\text{LSMO}} = 4\text{ nm}$, while for $t_{\text{LSMO}} = 8\text{ nm}$ the T_C and M_0 reduction is much smaller but still evident (see Fig. 2). No significant modifications are evidenced between uncapped and Au-capped LSMO thin films with $t_{\text{LSMO}} = 12\text{ nm}$.

We have performed a X-ray Photoemission Spectroscopy (XPS) study of Au-capped LSMO samples as a function of the gold layer thickness, to check for inter-

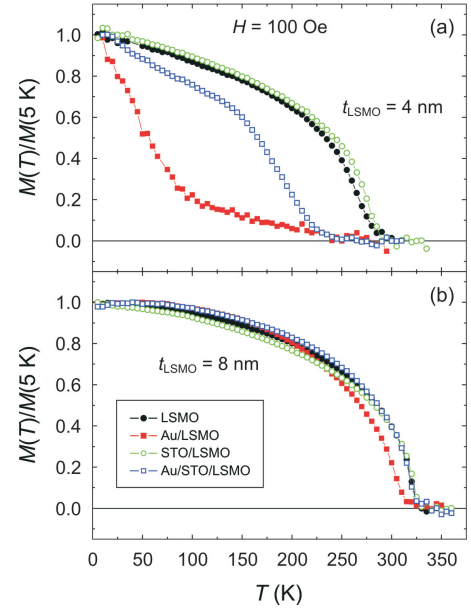


FIG. 2: (color online) Normalized magnetization vs. temperature curves measured by SQUID for different heterostructures: (a) LSMO thickness $t_{\text{LSMO}} = 4\text{ nm}$ or (b) $t_{\text{LSMO}} = 8\text{ nm}$. The STO and Au thickness is 2 nm.

diffusion of chemical species at the interface by monitoring the core photoemission lines and/or Auger peaks.²¹ The shape and position of the characteristic peaks from LSMO are essentially unchanged upon Au deposition, indicating the absence of relevant chemical reactions at the interface, at variance with what observed for Al on LSMO.¹⁹ Our results are consistent with recent x-ray absorption and circular dichroism spectroscopy data demonstrating that the deposition of Au on LSMO has no effect on the shape of the spectra collected at the Mn $L_{2,3}$ edges.²² No sizable interdiffusion of chemical species was detected beyond the instrumental sensitivity (about 10%) from the XPS peaks intensity trend vs. Au coverage. However, it must be noticed that the Curie temperature in LSMO is extremely sensitive to even small variations (a few percent) of the oxygen concentration,²³ so chemical effects on T_C or M_0 cannot be completely ruled out by our XPS analysis.

In order to suppress interdiffusion and interface chemical reactions, we have inserted a thin (2 nm-thick) STO film between the Au capping and the LSMO layer. STO is an insulating oxide with a very low lattice mismatch (0.8%) with respect to LSMO. Therefore, possible strain effects on the LSMO layer are minimized. Strain, in fact, is known to significantly alter the electronic properties of perovskite manganites.^{24,25,26,27} As one can see from Fig. 2 and Table I, the effects induced on both T_C and M_0 by a STO overlayer without gold capping are negligible. Therefore, the STO overlayer can be considered as inert.

The magnetic characterization performed by SQUID reveals that the Au/STO/LSMO multilayer with

TABLE I: Curie temperature T_C , Curie temperature shift ΔT_C and low temperature magnetization M_0 in LSMO thin films with and without Au and/or STO capping.

Sample	t_{LSMO} (nm)	T_C (K)	ΔT_C (K)	M_0 (emu/cm ³)
LSMO	4 ± 0.1	280 ± 5		420 ± 70
Au/LSMO	4 ± 0.1	95 ± 10	185 ± 11	150 ± 100
STO/LSMO	4 ± 0.1	285 ± 5	-5 ± 7	500 ± 70
Au/STO/LSMO	4 ± 0.1	220 ± 10	60 ± 11	420 ± 70
LSMO	8 ± 0.1	325 ± 2		590 ± 65
Au/LSMO	8 ± 0.1	315 ± 2	10 ± 3	420 ± 65
STO/LSMO	8 ± 0.1	325 ± 2	0 ± 3	480 ± 65
Au/STO/LSMO	8 ± 0.1	325 ± 2	0 ± 3	520 ± 65
LSMO	12 ± 0.1	345 ± 2		490 ± 50
Au/LSMO	12 ± 0.1	340 ± 2	5 ± 3	450 ± 50

$t_{\text{LSMO}} = 8$ nm and the corresponding uncapped LSMO film with the same thickness have, within the experimental uncertainty, the same T_C and M_0 values (see Table I). Conversely, the Au/STO/LSMO heterostructure with $t_{\text{LSMO}} = 4$ nm surprisingly still presents a large reduction ($\simeq 60$ K) of T_C .

As mentioned above, the manganite T_C reduction induced by the Au capping through the STO spacer at $t_{\text{LSMO}} = 4$ nm is not likely to be due to interdiffusion or strain. This conclusion is corroborated by the fact that, in this sample, M_0 is unaltered with respect to the value measured on uncapped LSMO layers. However, the presence of the STO spacer does not exclude space charge effects very close to the interface, although it may attenuate them. Local charge variations directly affect the electronic properties of LSMO. Apparently, magnetism is an extremely sensitive probe of these localized variations, whereas the usual voltage-drop signature of a con-

ventional Schottky barrier is strongly suppressed in this case by the reduced spatial extent, as demonstrated by the measured ohmic behavior of the Au/LSMO junctions. Interfacial modifications are naturally most effective on very thin films and this might be the reason why the effects of the Au capping layer are reduced in the samples with $t_{\text{LSMO}} = 8$ nm.

We would like to underline that the T_C reduction in Au- and Au/STO-capped LSMO thin films is very high compared to the field-induced T_C shifts (a few K) typically observed in field effect devices,¹⁵ and of the same order of magnitude of the T_p shifts (up to 130 K) induced by charge injection in p - n structures.⁵ This suggests that thin manganite films might be particularly suitable for devices where transport and magnetic properties could be tuned by the externally applied electric fields.

In summary, we have observed that capping $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films with gold has sizeable effects on the manganite Curie temperature and saturation magnetization at low temperature. These effects consist in a strong reduction of T_C and M_0 in Au-capped LSMO thin films with respect to uncoated LSMO films of the same thickness. For the thinnest (4 nm-thick) investigated LSMO film, a smaller but significant T_C reduction ($\simeq 60$ K) is observed even when an inert SrTiO_3 spacer is inserted between the gold film and the manganite layer. This finding suggests that the proximity effects induced by gold on the LSMO layer magnetic properties might have, at least partially, an electrostatic origin.

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- ¹ J. M. D. Coey, M. Viret, and S. von Molnár, Adv. Phys. **48**, 167 (1999).
- ² For a review, see C. H. Ahn, A. Bhattacharya, M. Di Ventra, J. N. Eckstein, C. Daniel Frisbie, M. E. Gershenson, A. M. Goldman, I. H. Inoue, J. Mannhart, A. J. Millis, A. F. Morpurgo, D. Natelson, and J.-M. Triscone, Rev. Mod. Phys. **78**, 1185 (2006).
- ³ H. Katsu, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **76**, 3245 (2000).
- ⁴ H. Tanaka, J. Zhang, and T. Kawai, Phys. Rev. Lett. **88**, 027204 (2002).
- ⁵ A. Tiwari, C. Jin, D. Kumar, and J. Narayan, Appl. Phys. Lett. **83**, 1773 (2003).
- ⁶ T. F. Zhou, G. Li, N. Y. Wang, B. M. Wang, and X. G. Lia, and Y. Chen, Appl. Phys. Lett. **88**, 232508 (2006).
- ⁷ S. B. Ogale, V. Talyansky, C. H. Chen, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **77**, 1159 (1996).

- ⁸ Y. W. Xie, J. R. Sun, D. J. Wang, S. Liang, and B. G. Shen, J. Appl. Phys. **100**, 033704 (2006).
- ⁹ F. X. Hu and J. Gao, Appl. Phys. Lett. **88**, 132502 (2006).
- ¹⁰ A. M. Grishin, S. I. Khartsev, and P. Johnsson, Appl. Phys. Lett. **74**, 1015 (1996).
- ¹¹ S. Mathews, R. Ramesh, T. Venkatesan, J. Benedetto, Science **276**, 238 (1997).
- ¹² W. Wu, K. H. Wong, C. L. Mak, C. L. Choy, and Y. H. Zhang, J. Appl. Phys. **88**, 2068 (2000).
- ¹³ T. Wu, S. B. Ogale, J. E. Garrison, B. Nagaraj, Amlan Biswas, Z. Chen, R. L. Greene, R. Ramesh, T. Venkatesan, and A. J. Millis, Phys. Rev. Lett. **86**, 5998 (2001).
- ¹⁴ X. Hong, A. Posadas, and C. H. Ahn, Appl. Phys. Lett. **86**, 142501 (2005).
- ¹⁵ T. Kanki, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **89**, 242506 (2006).
- ¹⁶ W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, Nat. Mater. **6**, 348 (2007).

- ¹⁷ S. Altieri, H. L. Tjeng, F. C. Voogt, T. Hibma, O. Rogo-
janu, and G. Sawatzky, Phys. Rev. B **66**, 155432 (2002).
- ¹⁸ L. Mieville, D. Worledge, T. H. Geballe, R. Contreras, K.
Char, Appl. Phys. Lett. **73**, 1736 (1998).
- ¹⁹ A. Plecenik, K. Fröhlich, J. P. Espinós, J. P. Holgado, A.
Halabica, M. Pripko, and A. Gilabert, Appl. Phys. Lett.
81, 859 (2002).
- ²⁰ R. Bertacco, M. Riva, M. Cantoni, L. Signorini and F.
Ciccacci, Appl. Phys. Lett. **86**, 252502 (2005)
- ²¹ D. Petti et. al., unpublished.
- ²² S. Stadler, Y. U. Idzerda, Z. Chen, S. B. Ogale, and T.
Venkatesan, J. Appl. Phys. **87**, 6767 (2000).
- ²³ A. M. De Léon-Guevara, P. Berthet, J. Berthon, F. Millot,
A. Revcolevschi, A. Anane, C. Dupas, K. Le Dang, J. P.
Renard, and P. Veillet, Phys. Rev. B **56**, 6031 (1997).
- ²⁴ A. J. Millis, Nature **392**, 147 (1998).
- ²⁵ K. H. Ahn, T. Lookman, and A. R. Bishop, Nature **428**,
401 (2004)
- ²⁶ C. Thiele, K. Dörr, O. Bilani, J. Rödel, and L. Schultz,
Phys. Rev. B **75**, 054408 (2007).
- ²⁷ A. Tebano, C. Aruta, P. G. Medaglia, F. Tozzi, G.
Balestrino, A. A. Sidorenko, G. Allodi, R. De Renzi, G.
Ghiringhelli, C. Dallera, L. Braicovich, N. B. Brookes,
Phys. Rev. B **74**, 245116 (2006).